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Method for the preparation of lower olefins by steam cracking

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METHOD FOR THE PREPARATION OF LOWER OLEFINES  
BY STEAM CRACKING

5

The present invention relates to a method for the preparation of lower olefines by steam cracking of heavy hydrocarbons obtained by Fischer-Tropsch synthesis in a naphtha designed steam cracking furnace.

10 In US 4,833,170 a process is described for the production of heavier hydrocarbons from one or more gaseous light hydrocarbons. Such hydrocarbons may be used as gas oil.

The present invention relates to the use of such heavy Fischer-Tropsch hydrocarbons for the preparation of  
15 lower olefines. For such preparation according to the invention use is made of new or available steam cracking furnace that is designed for steam cracking naphtha. Although naphtha and Fischer-Tropsch heavy hydrocarbons have different compositions, and different boiling point ranges a naphtha  
20 designed steam cracking furnace turned out to be suitable for steam cracking heavy Fischer-Tropsch hydrocarbons.

Accordingly, these heavy Fischer-Tropsch hydrocarbons may be used according to the invention for the preparation of lower olefines by steam cracking. Due to the difference in  
25 composition of the heavy Fischer-Tropsch hydrocarbons in comparison to naphtha, the lower olefines produced by steam cracking comprise less aromatic compounds and thus for producing the same amount of lower olefines less feed is required. In addition relative to steam cracking of naphtha,  
30 steam cracking of Fischer-Tropsch heavy hydrocarbons resulted in an increased production of ethene, propene, butene and a lower production of hydrogen, methane and carbon monoxide.

Accordingly, the present invention provides a method for the preparation of lower olefines by steam cracking,  
35 wherein

the feed comprises heavy hydrocarbons obtained by Fischer-Tropsch synthesis are subjected to steam cracking in

a naphtha designed steam cracking furnace for steam cracking the Fischer-Tropsch hydrocarbons into the lower olefines.

Preferably, the steam cracking of Fischer-Tropsch heavy hydrocarbons is carried out in a conventional naphtha  
5 designed steam cracking furnace comprises a convection zone provided a first preheating zone in which the Fischer-Tropsch feed is heated, a second preheating zone in which the heated Fischer-Tropsch hydrocarbons are heated in the presence of  
10 steam to form a mixture of liquid and gaseous Fischer-Tropsch hydrocarbons; and a super heating zone in which the liquid and gaseous Fischer-Tropsch hydrocarbons are super heated; and a cracking zone in which the gaseous super heated Fischer-Tropsch hydrocarbons are steam cracked into the lower  
olefines.

15 The initial and final boiling point of naphtha are lower than the initial and final boiling point of the heavy Fischer-Tropsch hydrocarbons. This may have as an effect that the feed to the second preheating zone is not a gas but is still a mixture of gas and liquid. Generally, the feed for  
20 the second preheating zone comprises less than 50 wt.% liquid Fischer-Tropsch hydrocarbons. Preferably this feed comprises less than 25 wt.% or more preferably less than 10 wt.% liquid Fischer-Tropsch hydrocarbons. Leaving the second preheating step the Fischer-Tropsch hydrocarbons are generally in the  
25 gas phase.

The cracking of the heavy Fischer-Tropsch hydrocarbons is carried out in the presence of steam and optionally in the presence of additional dilution gas. Generally, the weight ratio of steam to Fischer-Tropsch  
30 hydrocarbons is 0.4-0.8, preferably 0.5-0.75, more preferably 0.60-0.70.

Generally, the Fischer-Tropsch hydrocarbons used as a feed for steam cracking in the naphtha designed steam cracking furnace have an initial boiling point of 100 °C,  
35 preferably 150 °C, more preferably 200 °C, and a final boiling point of 380 °C, preferably 370 °C, more preferably 360 °C.

Generally, these Fischer-Tropsch heavy hydrocarbons comprise n-paraffines for 75 wt.%, preferably 80 wt.%, more preferably 90 wt.%. These n-paraffines have generally a carbon number of 5-25, preferably of 7-23, more preferably of 10-20.

The Fischer-Tropsch hydrocarbons to be used as a feed according to the invention may be directly obtained by the Fischer-Tropsch synthesis or indirectly after further treatment. Such a treatment may comprise fractional distillation of hydrocarbons originating from the Fischer-Tropsch synthesis. Such fractional distillation may be carried out at temperatures of 100-380 °C, preferably at 150-370 °C, and more preferably at 200-360 °C. An other pretreatment comprises hydro cracking of Fischer-Tropsch hydrocarbons, or by thermal cracking of Fischer-Tropsch hydrocarbons, which hydro cracking or thermal cracking provide the heavy Fischer-Tropsch hydrocarbons as described above.

It is a preferred characteristic of the heavy Fischer-Tropsch hydrocarbons that they are essentially free of aromatic compounds, nitrogen comprising compounds and sulphur comprising compounds.

The Fischer-Tropsch heavy hydrocarbons to be used according to the invention as a feed for steam cracking in a naphtha designed steam cracking furnace for the production of lower olefines, are produced in a Fischer-Tropsch synthesis. Fischer-Tropsch synthesis of hydrocarbons is a well known process. In the Fischer-Tropsch synthesis the starting material is a hydrocarbonaceous feed.

The hydrocarbonaceous feed suitably is methane, natural gas, associated gas or a mixture of C1-4 hydrocarbons. The feed comprises mainly, i.e. more than 90 v/v%, especially more than 94%, C1-4 hydrocarbons, especially comprises at least 60 v/v percent methane, preferably at least 75 percent, more preferably 90 percent. Very suitably

natural gas or associated gas is used. Suitably, any sulphur in the feedstock is removed.

The Fischer-Tropsch hydrocarbons generally  $C_4$ - $C_{100}$ , preferably  $C_4$ - $C_{50}$  hydrocarbons. Normally liquid Fischer-Tropsch hydrocarbons are suitably  $C_5$ -25 hydrocarbons, especially  $C_7$ -23 hydrocarbons, more especially  $C_{10}$ -20 hydrocarbons, or mixtures thereof. These hydrocarbons or mixtures thereof are liquid at temperatures between 5 and 30 °C (1 bar), especially at about 20 °C (1 bar), and usually are paraffinic of nature, while up to 24 wt%, preferably up to 12 wt%, of either olefines or oxygenated compounds may be present. Depending on the catalyst and the process conditions used in the Fischer Tropsch reaction, normally gaseous hydrocarbons, normally liquid hydrocarbons and optionally normally solid hydrocarbons are obtained. It is preferred to obtain a large fraction of normally solid hydrocarbons. These solid hydrocarbons may be obtained up to 85 wt % based on total hydrocarbons, usually between 50 and 75 wt %.

The partial oxidation of this hydrocarbons feed, producing mixtures of especially carbon monoxide and hydrogen, can take place according to various established processes. These processes include the Shell Gasification Process. A comprehensive survey of this process can be found in the Oil and Gas Journal, September 6, 1971, pp 86-90.

The oxygen containing gas is air (containing about 21 vol. percent of oxygen), oxygen enriched air, suitably containing up to 70 percent, or substantially pure air, containing typically at least 95 vol. % oxygen. Oxygen or oxygen enriched air may be produced via cryogenic techniques, but could also be produced by a membrane based process, e.g. the process as described in WO 93/06041. The boiler provides the power for driving at least one air compressor or separator of the air compression/separating unit.

To adjust the H<sub>2</sub>/CO ratio in the syngas, carbon dioxide and/or steam may be introduced into the partial oxidation process. Preferably up to 15% volume based on the amount of syngas, preferably up to 8% volume, more preferable up to 4% volume, of either carbon dioxide or steam is added to the feed. Water produced in the hydrocarbon synthesis may be used to generate the steam. As a suitable carbon dioxide source, carbon dioxide from the effluent gasses of the expanding/combustion step may be used. The H<sub>2</sub>/CO ratio of the syngas is suitably between 1.5 and 2.3, preferably between 1.8 and 2.1. If desired, (small) additional amounts of hydrogen may be made by steam methane reforming, preferably in combination with the water shift reaction. Any carbon monoxide and carbon dioxide produced together with the hydrogen may be used in the hydrocarbon synthesis reaction or recycled to increase the carbon efficiency. Additional hydrogen manufacture may be an option.

The percentage of hydrocarbonaceous feed which is converted in the first step of the process of the invention is suitably 50-99% by weight and preferably 80-98% by weight, more preferably 85-96% by weight.

The gaseous mixture, comprising predominantly hydrogen, carbon monoxide and optionally nitrogen, is contacted with a suitable catalyst in the catalytic conversion stage, in which the hydrocarbons are formed. Suitably at least 70 v/v% of the syngas is contacted with the catalyst, preferably at least 80%, more preferably at least 90, still more preferably all the syngas.

The catalysts used in for the catalytic conversion of the mixture comprising hydrogen and carbon monoxide are known in the art and are usually referred to as Fischer-Tropsch catalysts. Catalysts for use in the Fischer-Tropsch hydrocarbon synthesis process frequently comprise, as the

catalytically active component, a metal from Group VIII of the Periodic Table of Elements. Particular catalytically active metals include ruthenium, iron, cobalt and nickel. Cobalt is a preferred catalytically active metal.

5           The catalytically active metal is preferably supported on a porous carrier. The porous carrier may be selected from any of the suitable refractory metal oxides or silicates or combinations thereof known in the art. Particular examples of preferred porous carriers include  
10 silica, alumina, titania, zirconia, ceria, gallia and mixtures thereof, especially silica and titania.

          The amount of catalytically active metal on the carrier is preferably in the range of from 3 to 300 pbw per 100 pbw of carrier material, more preferably from 10 to 80  
15 pbw, especially from 20 to 60 pbw.

          If desired, the catalyst may also comprise one or more metals or metal oxides as promoters. Suitable metal oxide promoters may be selected from Groups IIA, IIIB, IVB, VB and VIB of the Periodic Table of Elements, or the  
20 actinides and lanthanides. In particular, oxides of magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, cerium, titanium, zirconium, hafnium, thorium, uranium, vanadium, chromium and manganese are most suitable promoters. Particularly preferred metal oxide promoters for  
25 the catalyst used to prepare the waxes for use in the present invention are manganese and zirconium oxide. Suitable metal promoters may be selected from Groups VIIB or VIII of the Periodic Table. Rhenium and Group VIII noble metals are particularly suitable, with platinum and palladium being  
30 especially preferred. The amount of promoter present in the catalyst is suitably in the range of from 0.01 to 100 pbw, preferably 0.1 to 40, more preferably 1 to 20 pbw, per 100 pbw of carrier.



The catalytically active metal and the promoter, if present, may be deposited on the carrier material by any suitable treatment, such as impregnation, kneading and extrusion. After deposition of the metal and, if appropriate, the promoter on the carrier material, the loaded carrier is typically subjected to calcination at a temperature of generally from 350 to 750 °C, preferably a temperature in the range of from 450 to 550 ° C. The effect of the calcination treatment is to remove crystal water, to decompose volatile decomposition products and to convert organic and inorganic compounds to their respective oxides. After calcination, the resulting catalyst may be activated by contacting the catalyst with hydrogen or a hydrogen-containing gas, typically at temperatures of about 200 to 350 °C.

The catalytic conversion process may be performed under conventional synthesis conditions known in the art. Typically, the catalytic conversion may be effected at a temperature in the range of from 100 to 600 °C, preferably from 150 to 350 °C, more preferably from 180 to 270 °C. Typical total pressures for the catalytic conversion process are in the range of from 1 to 200 bar absolute, more preferably from 10 to 70 bar absolute. In the catalytic conversion process mainly (at least 70 wt%, preferably 90 wt% of C5+ hydrocarbons are formed.

Preferably, a Fischer-Tropsch catalyst is used, which yields substantial quantities of normal (and also iso-) paraffins, more preferably substantially normal paraffins. A part may boil above the boiling point range of heavy hydrocarbons to normally solid hydrocarbons. A most suitable catalyst for this purpose is a cobalt-containing Fischer-Tropsch catalyst. The term heavy hydrocarbons as used herein, is a reference to hydrocarbon mixtures of which the boiling point range corresponds substantially to that of kerosene and

gas oil fractions obtained in a conventional atmospheric distillation of crude mineral oil. The boiling point range of these heavy hydrocarbons (also called middle distillates) generally lies within the range of about 100 - 380 °C, preferably 200 - 370 °C, more preferably 150 - 360 °C.

The higher boiling range paraffinic hydrocarbons may be subjected to a catalytic hydrocracking step or thermal cracking, which are known per se in the art, to yield the desired heavy hydrocarbons. The catalytic hydro-cracking is carried out by contacting the paraffinic hydrocarbons at elevated temperature and pressure and in the presence of hydrogen with a catalyst containing one or more metals having hydrogenation activity, and supported on a carrier. Suitable hydrocracking catalysts include catalysts comprising metals selected from Groups VIB and VIII of the Periodic Table of Elements. Preferably, the hydrocracking catalysts contain one or more noble metals from group VIII. Preferred noble metals are platinum, palladium, rhodium, ruthenium, iridium and osmium. Most preferred catalysts for use in the hydro-cracking stage are those comprising platinum.

The amount of catalytically active metal present in the hydrocracking catalyst may vary within wide limits and is typically in the range of from about 0.05 to about 5 parts by weight per 100 parts by weight of the carrier material.

Suitable conditions for the catalytic hydrocracking are known in the art. Typically, the hydrocracking is effected at a temperature in the range of from about 175 to 400 °C. Typical hydrogen partial pressures applied in the hydrocracking process are in the range of from 10 to 250 bar.

The process may be operated in a single pass mode ("once through") or in a recycle mode. The process may be carried out in one or more reactors, either parallel or in series. In the case of small hydro-carbonaceous feedstock

streams, the preference will be to use only one reactor. Slurry bed reactors, ebulliating bed reactors and fixed bed reactors may be used, the fixed bed reactor being the preferred option.

- 5           The production of lower olefines, in particular ethene and propene, is in general achieved by pyrolyzing the heavy Fischer-Tropsch hydrocarbons.

Pyrolysis is also called steam cracking and comprises thermal cracking of these hydrocarbons in the presence of  
10 steam and if desired a dilution gas. The process comprises a convection zone, a cracking zone, a cooling zone and a separation zone. The pyrolysis furnace comprises the convection zone and the cracking zone. The convection zone comprises a first preheating zone and a second preheating  
15 zone. Generally, feed is heated in the first preheating zone, and dilution gas is added to the feed before the (liquid and gas) mixture of feed and dilution gas is sent to the second preheating zone.

Naphtha furnaces designed for treating a naphtha feed  
20 will have a larger heat transfer surface area in the first preheating zone than furnaces designed for light feed as a heavy feed have a higher initial boiling point than light feed and the main aim of the first preheating zone is vapourizing (part of) the feed and heating the feed.

25           A furnace designed for treating gaseous feed, will have a smaller heat transfer surface area in the first preheating zone than a furnace designed for liquid feed as a gaseous feed does not need to be vapourized.

It is to be understood that the scope of the steam  
30 cracking process may include any number and types of process steps between each described process step or between a described source and destination within a process step.

Usually and preferably, all product of a process step will be subjected to the next process step. However, it is possible to send only part of the product of a process step to the next process step.

5           Feed can be introduced into the process at further inlets besides the standard inlet and the inlet where feed is introduced together with steam and/or dilution gas. However, it is preferred to introduce feed only at the standard inlet of the convection zone and further feed together with steam  
10 and/or dilution gas.

Dilution gas can be added at a single inlet, or can be added via several inlets. However, it is preferred to add dilution gas at a single inlet.

15           The temperatures mentioned in this specification are the temperatures which the feed attains.

20           The initial boiling point of naphtha can be of from 0 to 100 °C while final boiling points can range of from 90 to 250 °C. The initial and final boiling points ranges of the Fischer-Tropsch hydrocarbons are shifted to higher temperatures.

25           The convection zone generally comprises a first preheating zone and a second preheating zone between which is located an inlet for steam and optionally dilution gas. In the first preheating zone, the feed is heated. After the first preheating zone, steam and optionally dilution gas is added to the feed and the mixture obtained can be heated further in the second preheating zone to a temperature just below the temperature at which cracking starts to occur. The temperature of the product obtained from the convection zone  
30 will usually be of from 400 to 800 °C, depending upon the feed, more specifically of from 450 to 750 °C.

The pyrolysis furnace may be any type of conventional olefines pyrolysis furnace designed for pyrolyzing heavy feed

and operated for production of lower boiling products such as olefines, especially including a tubular steam cracking furnace. The tubes within the convection zone of the pyrolysis furnace may be arranged as a bank of tubes in parallel, or the tubes may be arranged for a single pass of the feedstock through the convection zone. Within each bank, the tubes may be arranged in a coil or serpentine type arrangement. At the inlet, the feed may be split among several tubes, or may be fed to one single pass tube through which all the feed flows from the inlet to the outlet of the first stage preheater. Preferably, the first and/or second preheating zone of the convection zone comprise a multiple pass tubular reactor in which feed is passed through the first and/or the second preheating zone via more than one tube. Multiple pass tubular reactors often contain tubes having connections at their ends leading feed from the one tube to the next tube until the feed is sufficiently heated to be mixed with dilution gas and be passed to the second preheating zone, or to be sent to the cracking zone.

20----- The pressure and temperature at which the feed is fed to the inlet of the first preheating zone is not critical, typically the temperature will be of from 0 to 300 °C.

The optimal temperature to which the feed is heated in the first preheating zone will depend upon the pressure of the feed, and the performance and operation of the remainder of the process. The product of the first preheating zone will generally have an exit temperature of at least 150 °C such as 195 °C. The upper range on the temperature of the feed in the first preheating zone is limited to the point at which the stability of the feed is impaired. At a certain temperature, the coking propensity of the feed increases. This temperature limit would apply to both the first and the second preheating zone and all tubes in these zones. Preferably, the exit

temperature of the feed within the first preheating zone is not more than 520 °C, and most preferably not more than 500 °C.

The heating elements in the first and second  
5 preheating zone in the convection zone is typically a bank of tubes, wherein the contents in the tubes are heated primarily by convective heat transfer from the combustion gas exiting from the cracking zone of the pyrolysis furnace, so-called flue gas. However, different heating elements can be used as  
10 well.

The pressure within the first and second preheating zone is not particularly limited. The pressure is generally within a range of from 4 to 21 bar, more preferably of from 5 to 13 bar.

15 In the process of the present invention part of the heavy hydrocarbons obtained by Fischer-Tropsch synthesis as the feed is introduced via the standard feed inlet of the convection zone, and if desired part of the feed is introduced further downstream in the convection zone.

20 Steam gas is added to the convection zone. This can be done preferably in or before the second preheating zone of the convection zone. Other dilution gas is preferably added at a point external to the pyrolysis furnace for ease of maintaining and replacing equipment.

25 The dilution gas is a vapour at the injection point into the convection zone. Examples of dilution gases are methane, ethane, nitrogen, hydrogen, natural gas, dry gas, refinery off gases, and a vapourized naphtha. Preferably, the steam is superheated steam.

30 Typical dilution gas temperatures at the dilution gas/feed junction range of from 140 °C to 800 °C, more preferably of from 150 °C to 780 °C, more preferably of from 200 to 750 °C.

The pressure of dilution gas is not particularly limited, but is preferably sufficient to allow injection. Typical dilution gas pressures added to the crude oil is generally within the range of from 6 to 15 bar.

5 It is desirable to add steam and optionally dilution gas between the first preheating zone and the second preheating zone in an amount which will generally be not more than 1 kg of dilution gas per kg of feed. However, there can be circumstances in which a higher amount of dilution gas can  
10 be advantageous.

The mixture of dilution gas and feed is fed to the second preheating zone where the mixture is heated further. The mixture generally comprises not more than 50 wt.% liquid Fischer-Tropsch hydrocarbons. Preferably not more than 25  
15 wt.%, most preferably not more than 10 wt.% Tubes of the second preheating zone can be heated by the flue gases from the cracking zone of the furnace. In the second preheating zone, the mix is fully preheated to near or just below a temperature at which substantial feedstock cracking and  
20 associated coke laydown in the preheater would occur such as 450 to 550 °C, preferably 460 - 500 °C, such as 490 °C.

Subsequently, the product of the convection zone is sent to the cracking zone. The temperature of the mixture of steam and feed is increased further under controlled  
25 residence time, temperature profile and partial pressure. The exit temperature of the product obtained in the cracking zone is generally of from 700 to up to 1000 °C. more specifically of from 750 to 950 °C. The pressure is generally within a range of from 2 to 25 bar, more preferably of from 3 to 18  
30 bar.

The reactions in the cracking zone are highly endothermic, and therefore a high rate of energy input is needed.

5 degradation by secondary reactions. Cooling of the product  
obtained in the cracking zone can be done in any way  
suitable, such as by direct quenching or indirect quenching.

10 can start at cooling where heavy components can be removed.  
Further, during cooling the gas obtained can be compressed,  
and acids and water can be removed. Subsequently, the product  
can be dried and uncracked feed, ethane and propane may be  
recovered for recycling as pyrolysis feed. The cracking  
15 severity affects the composition of the product obtained.

paraffinic, and aromatic products. Ethene generally is the predominant product, typically ranging from 15 to 60 %wt, based on the weight of the feed.

the last compressor stage, the gas is treated with caustic to remove hydrogen sulphide and carbon dioxide. Actetylenes may be hydrogenated with hydrogen-rich compressor gas. After the last compression stage, the cracked gas is typically dehydrated by chilling and dried by use of molecular sieves. Methane and hydrogen can be removed in a demethanizer. In a demethanizer, the hydrocarbons containing 2 carbon atoms are produced overhead and the hydrocarbons containing 3 carbon atoms or more is a bottom product. The overhead stream can be



hydrogenated to remove acetylene and then fractionated to produce ethene and ethane. The ethane can be recycled. The bottom product can be further fractionated, if appropriate, to remove heavy ends including compounds containing 4 carbon  
5 atoms or more. The overhead stream from a depropanizer can be hydrogenated to remove methylacetylene and propadiene, which can be recovered for sale or removed via other means. Propene can be obtained as overhead stream from the depropanizer, and the bottom propane fraction can be recycled.

10 Any percentage mentioned in this description is calculated on total weight or volume of the composition, unless indicated differently. When not mentioned, percentages are considered to be weight percentages. Pressures are indicated in bar absolute, unless indicated differently.

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CLAIMS

1. Method for the preparation of lower olefines by  
5 steam cracking, wherein

the feed comprises heavy hydrocarbons obtained by Fischer-Tropsch synthesis are subjected to steam cracking in a naphtha designed steam cracking furnace for steam cracking the Fischer-Tropsch hydrocarbons into the lower olefines.

10 2. Method as claimed in claim 1 wherein the nafta designed steam cracking furnace comprises a convection zone provided a first preheating zone in which the Fischer-Tropsch feed is heated, a second preheating zone in which the heated Fischer-Tropsch hydrocarbons are heated in the presence of  
15 steam to form a mixture of liquid and gaseous Fischer-Tropsch hydrocarbons; and a super heating zone in which the liquid and gaseous Fischer-Tropsch hydrocarbons are super heated; and a cracking zone in which the gaseous super heated Fischer-Tropsch hydrocarbons are steam cracked into the lower  
20 olefines.

3. Method as claimed in claim 2, wherein the feed for the second preheating zone comprises less than 50 wt.%, preferably less than 25 wt.%, more preferably less than 10 wt.% liquid Fischer-Tropsch hydrocarbons.

25 4. Method as claimed in claims 1-3, wherein the weight ratio of steam to Fischer-Tropsch hydrocarbons is 0.4-0.8, preferably 0.5-0.75, more preferably 0.60-0.70.

5. Method as claimed in claims 1-4, wherein the Fischer-Tropsch hydrocarbons have an initial boiling point of  
30 100 °C, preferably 150 °C, more preferably 200 °C, and a final boiling point of 380 °C, preferably 370 °C, more preferably 360 °C.

6. Method as claimed in claims 1-5, wherein the Fischer-Tropsch hydrocarbons comprise n-paraffines for 75  
35 wt.%, preferably 80 wt.%, more preferably 90 wt.%.

7. Method as claimed in claim 6, wherein the n-paraffines have a carbon number of 5-25, preferably 7-23, more preferably 10-20.

8. Method as claimed in claims 1-7, wherein the  
5 Fischer-Tropsch hydrocarbon feed is obtainable by fractional distillation of hydrocarbons originating from a Fischer-Tropsch synthesis at a temperature of 100-380 °C, preferably 150-370 °C, and more preferably at 200-360 °C, by hydro  
10 cracking of Fischer-Tropsch hydrocarbons, or by thermal cracking of Fischer-Tropsch hydrocarbons.

9. Method as claimed in claims 1-8, wherein the Fischer-Tropsch hydrocarbons are essentially free of aromatic compounds, N-compounds and/or S-compounds.

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